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LASER DETECTION OF CHEMICAL AGENTS(U) STANFORD UNIV CA  
R N ZARE 12 NOV 84 ARO-20527. 2-CH DAA229-83-K-0150

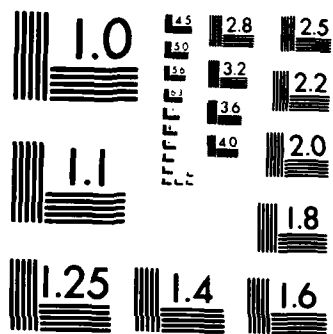
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The laser multiphoton ionization (MPI) technique has been used as a probe of molecules adsorbed on a quartz substrate. A detectability limit of less than $4 \times 10^{13}$ molecules of dimethyl methyl phosphonate (DMMP) corresponding to an exposure to a DMMP partial pressure of $1 \times 10^{-7}$ Torr for 1 second has been demonstrated. Efforts to make time-of-flight MPI photoelectron spectroscopy a quantitative tool have proved unsuccessful because of poor energy resolution. Efforts to detect phosphonates through a combination of microcolumn high pressure liquid chromatography (HPLC) in conjunction with laser fluorescence detection.		

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appear extremely promising. Using coumarin derivatization of the hydrolysis products of a number of common chemical warfare agents it has been possible to detect less than 1 picomole each of ethylmethylphosphonic acid, isopropylmethylphosphonic acid, and pinacolmethylphosphonic acid. Originator

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Laser Detection of Chemical Agents

Final Report

Richard N. Zare

November 12, 1984

U. S. Army Research Office

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## REPORT

Laser multiphoton ionization (MPI) has made it possible to ionize numerous species by a nonlinear process in which more than one visible ultraviolet photon is absorbed. It is useful to distinguish two classes of MPI processes, resonant and non-resonant. In the former, the molecule makes transitions to real states with lifetimes on the order of  $10^{-9}$  -  $10^{-6}$  seconds, while in the latter the transitions involve so-called virtual states with lifetimes of  $\sim 10^{-15}$  sec. As a consequence, resonant enhanced multiphoton ionization (REMPI) is about  $10^6$  times more sensitive while nonresonant MPI can be used as a "universal" detector. As another consequence REMPI requires laser powers of  $\sim \text{MW}/\text{cm}^2$ , NR MPI powers of  $\sim \text{GW}/\text{cm}^2$ . For quite some time MPI has been used to detect and investigate gas-phase species. The purpose of this study was to apply MPI for the detection of trace compounds adsorbed on surfaces. In our scheme the laser beam causes ionization on the surface. The laser radiation does not desorb species of interest which are ionized on passing through a focal region. Perhaps, superior results may be obtained in future experiments by separating the desorption step from the ionization step, and efforts are under way to explore this variation.

The experimental apparatus consists of an 8 mm quartz light pipe which passes from outside our vacuum systems into the ion source of a quadrupole mass spectrometer (Finnigan Model 3000). Laser light from a  $\text{Nd}^{+3}:\text{YAG}$  pumped, doubled dye laser (Quanta-Ray DCR-1 and PDL with Lasermetrics KD\*P crystals) was mildly focused into the light pipe, and ionized molecules adsorbed on the light pipe face within the mass spectrometer source. The vacuum chamber is maintained at a base pressure of less than  $1 \times 10^{-7}$  Torr. Dimethyl methyl phosphenate (DMMP) (Aldrich, 97%) undergoes several freeze-pump-thaw cycles before being admitted into the vacuum chamber through a needle valve and effusive jet.

Figure 1 shows the mass spectrum obtained from the surface at a pressure of  $4 \times 10^{-6}$  Torr, using a laser wavelength of 265 nm. Gas-Phase ionization of DMMP under similar conditions is negligible. A comparison with the mass spectrum obtained with electron impact ionization (Figure 2) makes a most compelling case against Figure 1 being the result of electron-mediated ionization. Excitation at  $\lambda = 290$  nm shows extensive fragmentation, reflecting the fact that the ionization is now a 4-photon process.

The above results were obtained with the laser operating at 10 Hz. Upon converting the observed signal versus pressure to signal versus exposure, we conclude we are able to detect  $\leq 4 \times 10^{13}$  molecules of DMMP, corresponding to an exposure of  $1 \times 10^{-7}$  Torr of DMMP for 1 second. Further work is needed to understand these surface MPI processes, but their high sensitivity is established by this study.

During this contract period we also investigated the use of the photoelectron kinetic energy spectrum as a characteristic signature of compounds. For this purpose it is necessary to find a calibration standard for our time-of-flight photoelectron spectrometer. We have investigated the use of atomic MPI using  $\text{Cr}(\text{CO})_6$  and  $\text{Fe}(\text{CO})_5$  as the convenient carrier gas. In general we find severe problems in obtaining a resolving power or absolute accuracy

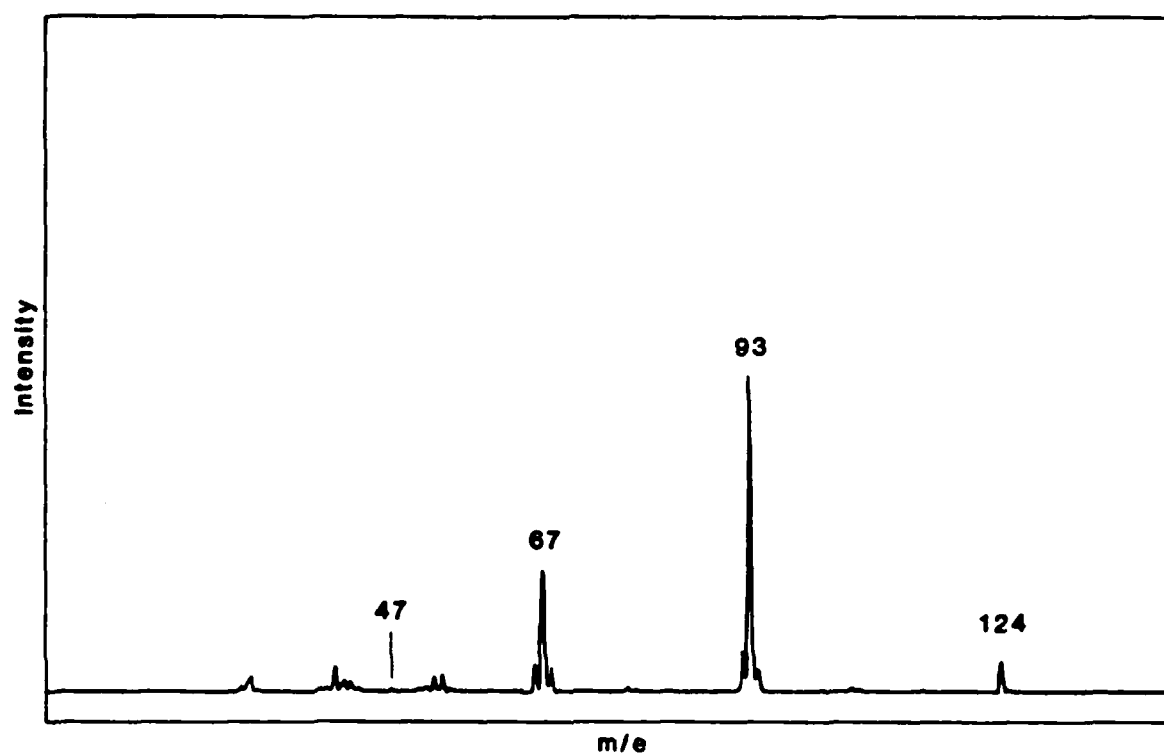


Figure 1. DMMP Mass Spectrum; Surface MPI  $\lambda = 265$  nm,  $P = 4 \times 10^{-6}$  Torr.

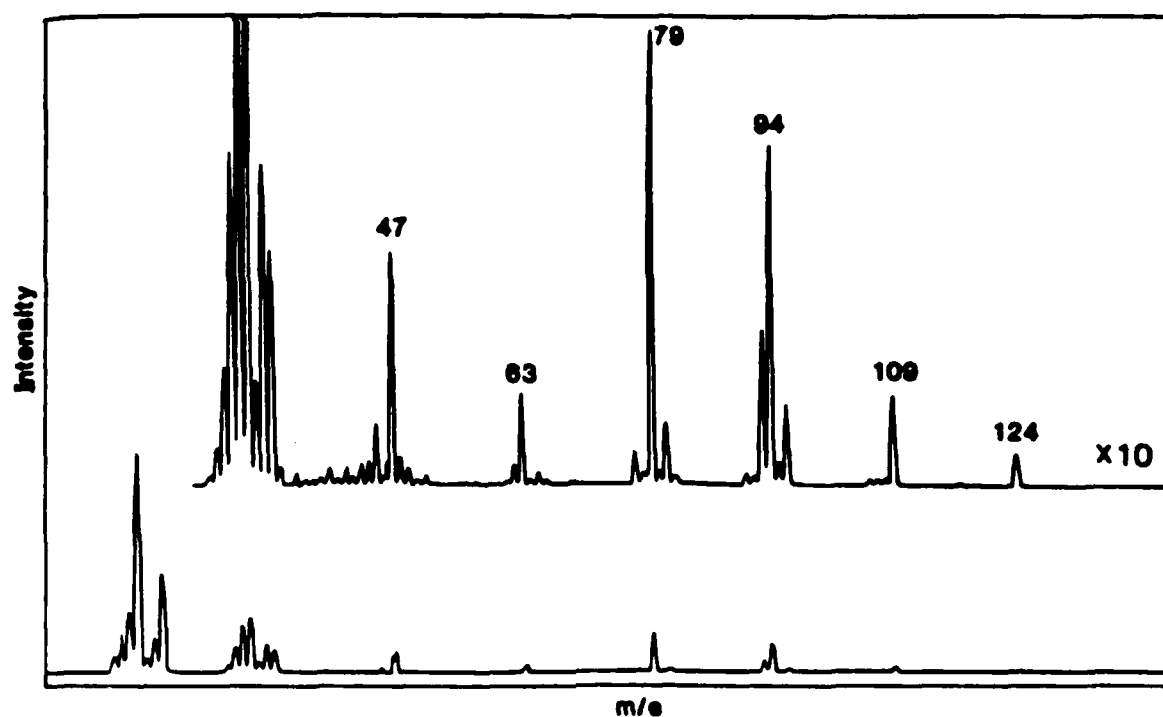


Figure 2. DMMP Mass Spectrum With Electron Impact Ionization; Electron Energy  $\sim 70$  eV,  $P = 4 \times 10^{-6}$  Torr.

better than 10 meV ( $80 \text{ cm}^{-1}$ ) although the reproducibility (precision) is deceptively high ( $\sim 1 \text{ meV}$ ). There appears to be major experimental problems caused by the build up of stray electric fields and the presence possibly of stray AC fields (rf fields) from the firing of the laser -- all of which distort and degrade electron trajectories.

At the very end of this contract we explored the use of microcolumn HPLC to separate and to detect phosphonates derivatized with 4-bromomethyl-7-methoxycoumarin. This label when attached readily fluoresces when exposed to the 325 nm radiation from a He-Cd laser. A preliminary chromatogram is displayed in Figure 3. This work would not have been possible without the direct assistance of Dr. Dennis Reutter, Dr. Paul Bossle, and their coworkers at CRDC, Aberdeen Proving Ground. Based on these results we are confident that a major improvement in the detection of phosphonates can be achieved by the use of laser fluorimetry in conjunction with microcolumn HPLC.

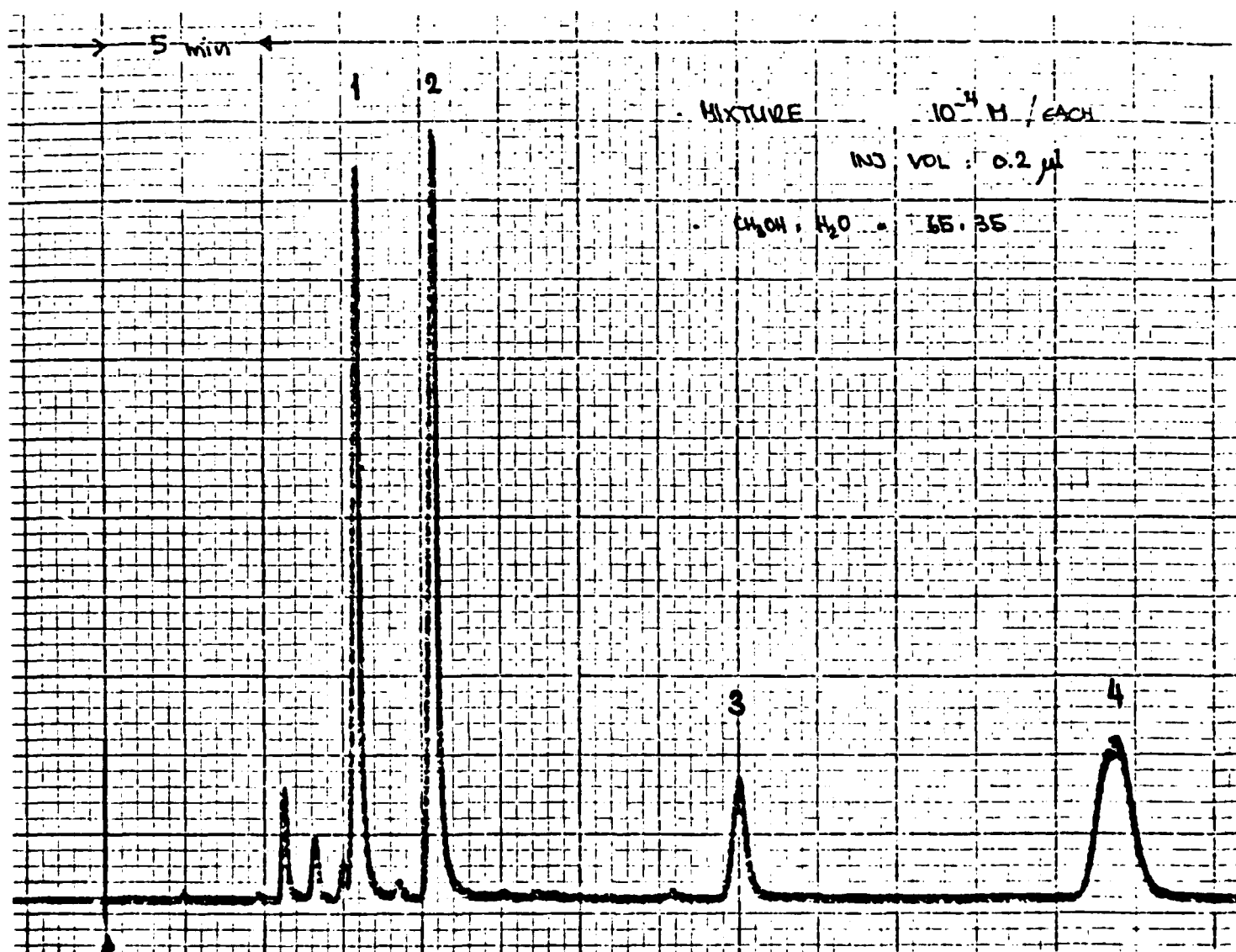


Figure 3. Chromatogram of coumarin-derivatized ethylmethylphosphonic acid (peak 1), isopropylmethylphosphonic acid (peak 2), pinacolylmethylphosphonic acid (peak 4) and unreacted label (peak 3).



## Appendix

### Publications

"MPI of Surface Adsorbed Molecules", Joseph L. Durant and Richard N. Zare,  
Department of Chemistry, Stanford University, Stanford, CA 94305, previously  
sent.

### Participating Scientific Personnel

Joseph Durant, Ph.D., received August, 1984

Sarah Williams

Charles Flowers

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